AD-A062 416   NAVAL RESEARCH LAB   WASHINGTON D C   F/G 4/2
                ON THE GROWTH OF AEROSOL PARTICLES WITH RELATIVE HUMIDITY.(U)
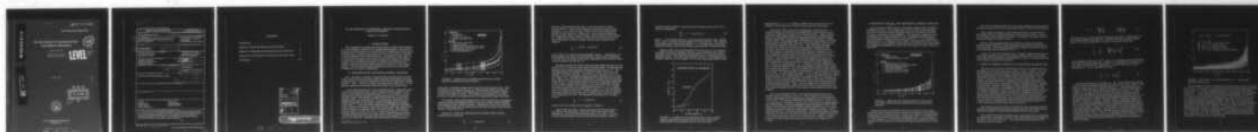   AUG 78   J W FITZGERALD

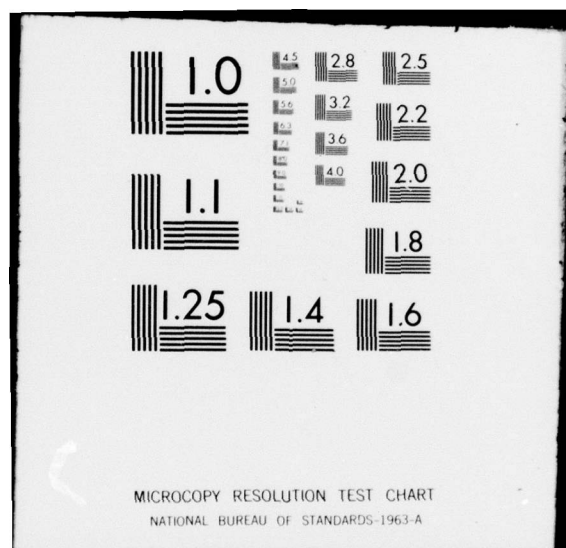UNCLASSIFIED   NRL-MR-3847   SBIE-AD-E000 236   NL

| OF |
AD
A062416

END
DATE
FILMED
3-79
DDC

1.0

4.5
50
56
63

2.8

2.5

3.2

2.2

3.6

1.1

4.0

2.0

1.8

1.25

1.4

1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

$\mathcal{R}_{\text{\tiny$\sim$}}$

AD-E 000 236

NRL Memorandum Report 3847

On the Growth of Aerosol Particles with Relative Humidity

(12)
NW

James W. Fitzgerald

Atmospheric Physics Branch
Ocean Sciences Division

LEVEL III

August 1978

NAVAL RESEARCH LABORATORY
Washington, D.C.

78 10 05 031

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Memorandum Report 3847	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ON THE GROWTH OF AEROSOL PARTICLES WITH RELATIVE HUMIDITY		5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL problem.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) James W. Fitzgerald		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, D.C. 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NRL Problem A03-14, Element 63797N, Task X0665/AA
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Naval Ocean Systems Center San Diego, CA 92152		12. REPORT DATE August 1978
		13. NUMBER OF PAGES 14
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Aerosols	Aerosol model
Aerosol growth	Aerosol composition
Relative humidity	Atmospheric aerosols
Aerosol measurements	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Previous work on the growth with relative humidity of sodium chloride and ammonium sulfate particles and of naturally occurring aerosols is reviewed. New measurements of aerosol particle growth with humidity obtained during a research cruise of the USNS Hayes to the North Atlantic and Mediterranean Sea in May 1977 are presented. A model which describes the observed variation in aerosol growth behavior from one air mass to another is developed.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73
S/N 0102-014-6601

i

CONTENTS

iii

78 10 05 031

ON THE GROWTH OF ATMOSPHERIC AEROSOL PARTICLES WITH RELATIVE HUMIDITY

James W. Fitzgerald

1. INTRODUCTION

The propagation of optical and infrared energy through the atmosphere is at times strongly affected by the suspended particulates. Since aerosol particles attenuate energy in an amount which is proportional to their cross sectional area, a subject of particular concern is the growth (or swelling) of aerosol particles with relative humidity. The purpose of this report is to review previous work on the growth of aerosol particles with relative humidity and to combine these results with physical reasoning to develop a model of aerosol particle growth with humidity which describes the observed variation in aerosol growth behavior from one air mass type to another. The variation in aerosol growth with humidity is attributable to differences in chemical composition.

2. BEHAVIOR OF NaCl AND MARINE AEROSOL PARTICLES

Fig. 1 presents a summary of theoretically and experimentally determined growth curves for both pure NaCl particles and naturally occurring marine aerosols. Plotted is the particle size ratio as a function of relative humidity. Here r is particle radius at the indicated humidity and r_0 is the particle radius at zero percent relative humidity (= dry particle size).

A pure NaCl particle will, with increasing humidity, experience practically zero growth until some critical value of relative humidity in the range 70-76% (shown by the hatched area in Fig. 1) is reached. At this humidity the particle undergoes a rapid phase transition to a saturated solution droplet. The relative humidity at which this transition occurs depends on the size of the particle. An NaCl aqueous solution droplet grows with humidity in the manner shown by the uppermost continuous curve in Fig. 1. This curve was computed by Low (1968) who used data on the variation with molality of the ionic activity coefficient, density and surface tension of an aqueous sodium chloride solution. Although this curve for NaCl is strictly for a 0.5-μm radius dry particle, it can be assumed without much loss of accuracy that at relative humidities below ~95-96% all NaCl particles with a dry radius in the range 0.05-5.0 μm grow at the same rate. Measurements have shown that there is some
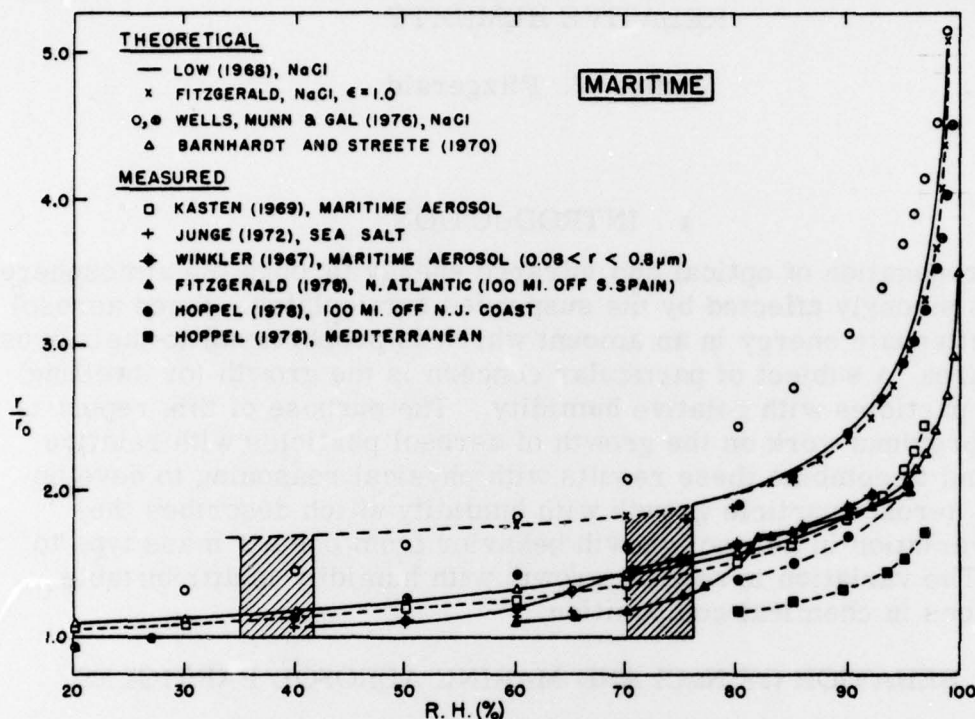
1

FIGURE 1. Measured and calculated growth curves for NaCl particles and natural marine aerosols.

hysteresis in the phase change of NaCl and other pure salt particles. Thus, on exposure to decreasing humidity an NaCl solution droplet will become supersaturated and will not crystallize until the relative humidity reaches a value in the range of 35-45%. The region for the transiton to dry NaCl particles is shown by the hatched area at the appropriate range of humidity.

The dashed curve passing through the x's was computed from the approximation formulas of Fitzgerald (1975) for the size-versus-relative humidity relationship for NaCl solution droplets. Comparison of this curve with that of Low (1968) shows that the approximation formula accurately describes the behavior of NaCl particles.

Wells et al. (1976) have approximated the growth of NaCl solution droplets by the expression

$$\frac{r}{r_0} = 1 - 0.9 \ln(1-S), \qquad (1)$$

2

where S is the saturation ratio and r_0 is the zero percent relative humidity radius. A plot of this equation is shown by the open circles in Figure 1. It is clear that Eq. (1) does not correctly describe the behavior of NaCl particles. Wells et al. make a distinction between the dry particle radius r_d and the radius at zero percent relative humidity. They define the dry radius to be the particle radius when S=0.27. If this distinction in radius is made, then the ratio of radius to dry radius is

$$\frac{r}{r_d} = 0.78[1 - 0.9\ln(1-S)] . \qquad (2)$$

A plot of Eq. (2) is shown by the symbol ⊗ in Figure 1. Although Eq. (2) underestimates the radius of NaCl particles at high relative humidities, it is clear that it provides a much better description of the growth of NaCl solution droplets than does Eq. (1).

Barnhardt and Streete (1970) have empirically fitted an equation to the growth curve of "sea salt" nuclei given by Wright (1939). Wright assumed a particle size-relative humidity relationship of the form $S = e^{A/r} - Q/r^3$. The exponential term expresses the effect of surface curvature on the equilibrium relative humidity. The quantity A in this term is not very sensitive to particle composition and was taken by Wright to have a value of 1.17×10^{-7} cm. The value of Q depends on the total mass of a particle and on the amount and chemical composition of soluble material contained in the particle. Using measurements of visibility (scattering coefficient) at 80% relative humidity from coastal sites in the British Isles, Wright arrived at an estimate of the average particle size at S = 0.8. Susbtitution of this value of particle radius and the value S = 0.8 into the expression for S yielded a value of Q. Wright's growth curve must be regarded as an approximation to the behavior of coastal nuclei, which he assumed were composed of sea salt. The Barnhardt and Streete fit to Wright's curve is

$$\frac{r}{r_o} = 1 - 0.36\ln(1-S) . \qquad (3)$$

A plot of Eq. (3) is shown by the triangles in Figure 1.

Junge (1972) has given a curve of the mass ratio versus relative humidity for sea salt nuclei. The mass ratio is the mass of water absorbed by a particle divided by the particle's dry mass. The size-versus-relative humidity curve for sea salt nuclei shown in Figure 1

3

(plotted using the symbol +) was derived from Junge's mass ratio curve using the relationship

$$\frac{r^3}{r_o^3} = 1 + m_w \rho_o / m_o \rho_w , \qquad (4)$$

where ρ_w is the density of water, m_w is the mass of water in the droplet and m_o and ρ_o are the mass and density of the dry particle. This relationship assumes that volumes are additive, i.e., that the volume of solution equals the volume of dry soluble matter plus the volume of absorbed water.

Winkler (1967) made measurements of the ratio m_w/m_o as a function of relative humidity on samples of aerosol mass collected on the Island of Helgoland in the North Sea during periods when the air trajectories were generally marine. The curve due to Winkler in Fig. 1 was computed from Winkler's data for the size range $0.08 < r \leq 0.8 \mu m$ using relationship (4) and
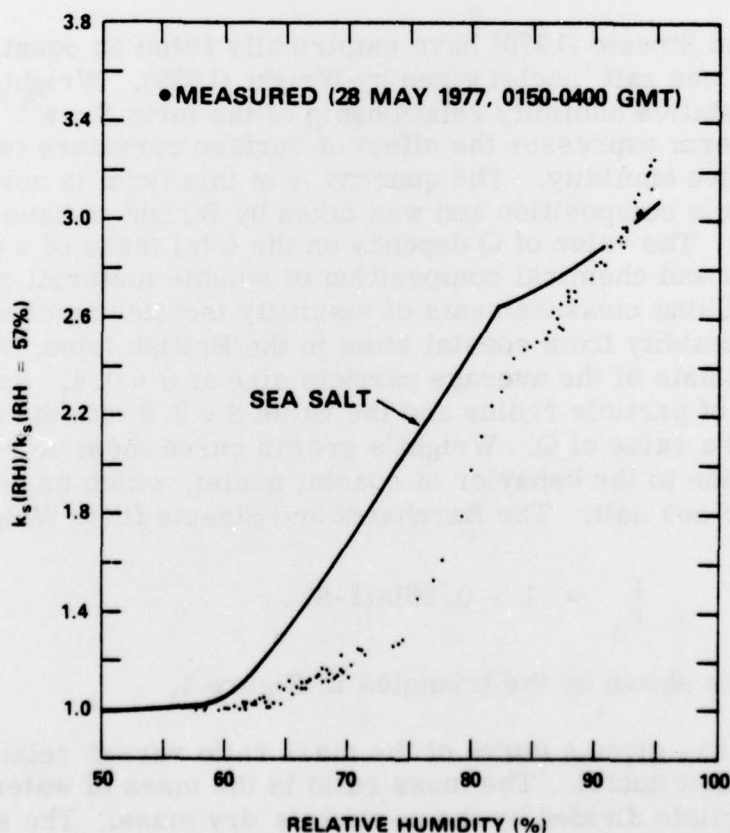

FIGURE 2. Comparison of the scattering ratio-versus-relative humidity relationship measured during the 1977 cruise of the USNS HAYES with a published curve for sea salt nuclei.

4

assuming that $\rho_O/\rho_W = 1.5$. Kasten's (1969) curve is an empirical fit to Winkler's data for particles in both the large and giant size range.

Fitzgerald's (1978) result for the dependence of particle size on relative humidity was inferred from nephelometer measurements of the scattering coefficient as a function of relative humidity. These measurements were made approximately 160 km off the coast of southern Spain during a transatlantic cruise of the USNS HAYES from Norfolk, Virginia to Rota, Spain. The measurements off Spain were made during a two-hour period (from 0150-0400 GMT, May 28, 1977) during which time the relative humidity increased from 57% to 95%. This increase in humidity occurred as a result of a simultaneous decrease in temperature and increase in dew point but was not accompanied by a frontal passage or any other change in conditions which would indicate a change in air mass. The instantaneous values of the scattering coefficient recorded at one minute intervals were divided by the scattering coefficient at 57% relative humidity. The resulting scattering ratios are plotted as a function of relative humidity in Fig. 2. A smooth curve fitted through these points was transformed into the growth curve (shown by the solid triangles) in Fig. 1 using the relationship $k_S \sim r^2$. A trajectory analysis indicated that the air mass had passed over the Iberian peninsula a couple of days earlier. For comparison purposes, Fig. 2 also shows the variation of light scattering ratio with humidity for natural sea spray nuclei, as measured by Pueschel et al. (1969). It is seen that both curves in Fig. 2 exhibit a change in slope in the range of 81 to 82% relative humidity. A plot of the scattering ratio versus relative humidity for a distribution of ammonium sulfate (an important constituent of many continental aerosols) particles will also show an inflection in the curve at about 81% relative humidity, which is the deliquescent point of bulk ammonium sulfate. Thus, one can probably find a mixture of sea salt nuclei and ammonium sulfate nuclei for which the computed scattering ratio-relative humidity curve is very similar to that measured off the coast of Spain.

The curves of Hoppel (1978) for the Mediterranean Sea and for the Atlantic Ocean off the coast of the U. S. were obtained by measuring the critical supersaturation of monodisperse atmospheric aerosol particles of a known size. This measurement permitted the quantity $B_O = i\epsilon\rho_O M_W/M_S \rho_W$ to be determined. The factor $i\epsilon\rho_O/M_S$ in B_O is the principal unknown appearing in theoretically derived relationships (Junge and McLaren, 1971; Fitzgerald, 1975) between relative humidity and the equilibrium size of solution droplets formed upon particles containing an insoluble component. In the expression for B_O, i is the van't Hoff factor, ϵ is the mass fraction of soluble material in the particle, M_W and M_S are the molecular weights of water and of the soluble salt and ρ_O and ρ_W are as defined above. Hoppel's measurements were made on particles having a dry radius in the range 0.07 to 0.10 μm.

5

3. BEHAVIOR OF $(NH_4)_2SO_4$ AND CONTINENTAL AEROSOL PARTICLES

Fig. 3 presents growth curves for ammonium sulfate nuclei and natural continental aerosols. The hatched area from 79 to 82% relative humidity shows the region where solid $(NH_4)_2SO_4$ particles will undergo the phase transition to saturated solution droplets. The uppermost continuous curve originating at 81% relative humidity is the relationship between particle size and relative humidity for the case of a pure (i. e., $\epsilon = 1.0$) ammonium sulfate particle, as computed by Low (1968). This particular curve is for a dry radius of 1.0 μm; however, the growth curves for other dry radius values will not depart significantly from this curve for values of relative humidity below 95%.
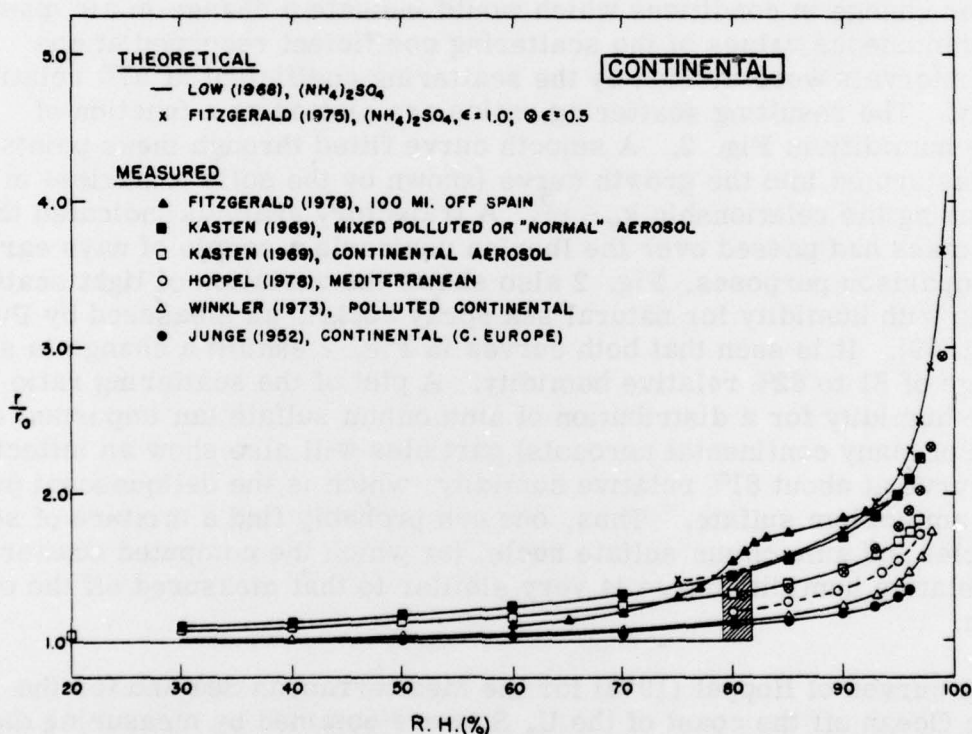

FIGURE 3. Measured and calculated growth curves for both ammonium sulfate particles and naturally occurring aerosol particles.

The growth curves indicated by the x's and circled x's are for pure ammonium sulfate particles and for particles composed of 50% ammonium sulfate and 50% insoluble material, respectively, and were computed from the approximation formulas given by Fitzgerald (1975). A dry radius of 1 μm was assumed. It is seen that the approximation formulas accurately describe the exact behavior of ammonium sulfate particles given by Low's curve.

The curves of Kasten (1969) for normal and continental aerosol particles represent empirical fits to data obtained by Winkler (1967) in central Europe.

Using a light microscope, Junge (1952) made direct measurements of the radius growth of individual particles in the giant size range. The results of these measurements for samples of atmospheric aerosols collected in central Europe are shown in Fig. 3.

Winkler (1973) measured the water uptake as a function of relative humidity of bulk samples of aerosol particles collected in polluted areas of central Europe. From these measurements he deduced the particle growth curve labeled polluted continental in Fig. 3.

Finally, we have also included in Fig. 3 Hoppel's Mediterranean growth curve and Fitzgerald's curve for the Atlantic Ocean off the coast of Spain since these curves are based on measurements made in air masses believed to be modified continental in character.

4. MODEL OF AEROSOL GROWTH AS A FUNCTION OF AIR MASS TYPE

There are two particularly noteworthy features of the growth curves of atmospheric aerosol particles shown in Figs. 1 and 3. Firstly, it is seen that atmospheric aerosol particles, unlike pure salt particles, show continuous smooth growth with changing relative humidity without any large and sudden increase in size at some critical value of humidity. This property of the growth curves of natural aerosol particles has been discussed by Winkler (1973) and is explained by the gradual deliquescence of soluble material which is present as a mixture of different salts. Secondly, it is seen that, basically, the amount of water absorbed with increasing humidity decreases as the continentality of the aerosol increases. This is probably attributable in part to the fact that continental aerosol particles are usually composed of a greater proportion of insoluble material than marine aerosol particles and in part to the fact that the ionic mixture forming the water soluble fraction is more complex in continental aerosol than in natural marine aerosols. Due to mutual interactions among ions, a given mass of a complex salt mixture will lower the vapor pressure to a much less degree than the same mass of pure salt.

We shall now proceed to derive a formula for the size-versus-relative humidity relationship of atmospheric aerosol particles which describes the observed variation in aerosol growth behavior with air mass type.

The equilibrium relative humidity over a salt solution can be expressed by Raoult's law, modified to account for the dissociation of ions through the inclusion of the van't Hoff factor. The linearized approximation to this expression may be written

$$S = 1 - i\frac{M_w}{M_s}\frac{m_s}{m_w} = 1 - i\epsilon\frac{M_w}{M_s}\frac{m_o}{m_w}, \tag{5}$$

where M_s and m_s are the molecular weight and dry mass, respectively, of the soluble fraction of the particle. The other symbols have been defined above. If we now combine Eqs. (4) and (5) we have the result that

$$\frac{r}{r_o} = \left[1 + \frac{i\epsilon M_w}{M_s}\frac{\rho_o}{\rho_w}\frac{1}{1-S}\right]^{\frac{1}{3}}. \tag{6}$$

The coefficient of the term $(1-S)^{-1}$ in Eq. (6) is a function of the composition of the aerosol particles and may, therefore, be regarded as a function of air mass type. We denote this coefficient by γ which we call the air mass characteristic. Eq. (6) may then be written

$$\frac{r}{r_o} = \left[1 + \frac{\gamma}{1-S}\right]^{\frac{1}{3}}. \tag{7}$$

 With a proper choice of the value of γ, Eq. (7) describes quite well the growth curves of atmospheric aerosol particles given in Figs. 1 and 3. Fig. 4 shows a plot of Eq. (7) for different values of γ. On one extreme, the behavior of NaCl droplets at relative humidities above 76% is described by a value of γ of 1.22. Below 76% relative humidity, the value $\gamma = 1.22$ yields a size dependence on humidity which is intermediate between the NaCl curves for increasing and decreasing humidity conditions (see Fig. 1). On the other extreme, Junge's curve for polluted continental aerosols is fitted by a value of γ of 0.061. The data in Fig. 3 indicate an upper limit of 0.17 for polluted continental aerosols. Between the extremes of pure NaCl nuclei and polluted continental aerosols we have defined three aerosol (or air mass) types. These are: Clean (natural) maritime; modified maritime; and modified continental. The ranges of γ for each of these aerosol categories given in Fig. 4 were selected to give reasonable fits to the aerosol growth curves in Figs. 1 and 3. As additional measurements of aerosol growth with humidity become available some change in the values of γ characterizing aerosol particles in different air masses will undoubtedly have to be made.

$$\frac{r}{r_0} = \left[1 + \frac{\gamma}{1-S}\right]^{\frac{1}{3}}, \quad \gamma = \text{AIR MASS CHARACTERISTIC}$$

- - - $\gamma = 1.22$ NaCl

$1.22 \geq \gamma > 0.76$, CLEAN (NATURAL) MARITIME

$0.76 \geq \gamma > 0.38$, MODIFIED MARITIME

$0.38 \geq \gamma > 0.17$, MODIFIED CONTINENTAL

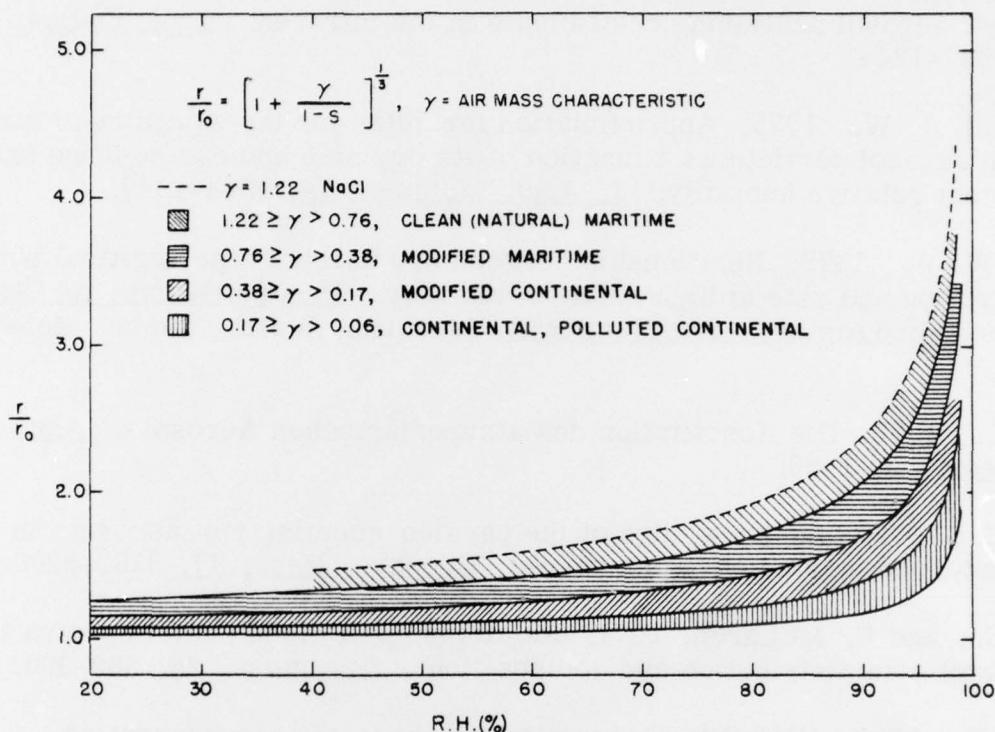$0.17 \geq \gamma > 0.06$, CONTINENTAL, POLLUTED CONTINENTAL

FIGURE 4. Plot of Eq. (7) for different values of γ, representing different aerosol types.

Since the effect of surface curvature was not taken into account in deriving Eq. (6), Eq. (7) will begin to overestimate the size of aerosol particles (having a dry radius 0.1 μm) by a significant amount at relative humidities above about 98.5%. Using sodium chloride particles as an example, the equilibrium size of a 0.1 μm dry radius particle will be overestimated by more than 5% for values of relative humidity exceeding 98.5% while the size of a 0.5-μm dry radius NaCl particle will be overestimated by Eq. (7) by more than 5% at relative humidities higher than 99.92%. In fact, Eq. (7) (as well as the size-relative humidity relationship of Wells et al. for NaCl, that of Barnhardt and Streete and of Kasten for maritime aerosols and that of Winkler for continental aerosols) predicts a value of r/r_0 of infinity for $S = 1$. It is also to be noted that Eq. (7) gives a limiting value of r/r_0 greater than unity when $S = 0$. However, it is clear from Figs. 1, 3 and 4 that in the range of 20 to 98% relative humidity, Eq. (7) provides a good description of the growth of atmospheric aerosol particles with humidity.

REFERENCES

Barnhardt, E. A., and J. L. Streete, 1970: A method for predicting atmospheric aerosol scattering coefficients in the infrared. Appl. Optics, 9, 1337-1344.

Fitzgerald, J. W., 1975: Approximation formulas for the equilibrium size of an aerosol particle as a function of its dry size and composition and the ambient relative humidity. J. Appl. Meteor., 14, 1044-1049.

Hoppel, W. A., 1978: Relationship between dry aerosol size, critical supersaturation and size at high relative humidity. Preprints Conf. on Cloud Physics and Atmospheric Electricity, Issaquah, Wash., Amer. Meteor. Soc.

Junge, C., 1952: Die Konstitution des atmosphärischen Aerosols. Ann. Meteor., 5, 1-55.

Junge, C., 1972: Our knowledge of the physico-chemistry of aerosols in the undisturbed marine environment. J. Geophys. Res., 77, 5183-5200.

Junge, C., and E. McLaren, 1971: Relationship of cloud nuclei spectra to aerosol size distribution and composition. J. Atmos., 28, 382-390.

Kasten, F., 1969: Visibility forecast in the phase of precondensation. Tellus, 21, 631-635.

Low, R. D. H., 1968: A comprehensive report on nineteen condensation nuclei. Part I. Equilibrium growth and physical properties. Rept. ECOM-5249, Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico, 553 pp.

Pueschel, R. F., R. J. Charlson, and N. C. Ahlquist, 1969: On the anomalous deliquescence of sea-spray aerosols. J. Appl. Meteor., 8, 995-998.

Wells, W. C., G. Gal, and M. W. Munn, 1977: Aerosol distributions in maritime air and predicted scattering coefficients in the infrared. Appl. Optics, 16, 654-659.

Winkler, P., 1967: Wachstum natürlichen Aerosolteilchenproben in Abhängigkeit von der relativen Feuchtigkeit. Master's Thesis, Univ. of Mainz, Mainz, W. Germany.

Winkler, P., 1973: The growth of atmospheric aerosol particles as a function of the relative humidity. II. An improved concept of mixed nuclei. Aerosol Sci., 4, 373-387.

Wright, H. L., 1939: Atmospheric opacity: A study of visibility observations in the British Isles. <u>Quart. J. Roy. Meteor. Soc.</u>, <u>65</u>, 411-439.